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STUDY OF AEROSPACE MATERIALS, COATINGS, ADHESIONS AND PROCESSES

COATING OF SELF-CATALYTIC NICKEL ON ALUMINUM

AND ALUMINUM ALLOYS

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PROTECTIVE AND PROTECTION SYSTEMS SECTION
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REPORT OF THE WORK CORRESPONDING TO THE 1st PHASE OF THE PROGRAM (PERIOD FROM JULY 15 1982 TO JULY 15 1983). CONTRACT ECARD 32+056.

Torrej**ó**n de Ardoz, Cotober 1983

TITLE: COATING OF SELF-CATALYTIC NICKEL ON ALUMINUM ALLOYS.

I - INTRODUCTIONS AND COJETIVES

'The self-catalytic deposition of nickel has been since some years ago an important objetive for many investigators, fully justified by itself due to the peculiar characteristics of the chemical process and to the technical applications derived from it.

In 1946, A. Murtz was able to verify that the aqueous solutions of nickel hypophosphite undergo a partial reduction when they are submitted to temperatures of about 1982.

Afterwards, P. Breteau, in 1911, was abla to demonstrate in the same way that the reduction is self-catalytic and that the reduced nickel contained phosphorus. The bibliography is abundant in this subject and it can be said that at the present time its study still continues to arouse interest, a great number of reducing agents have been studied and that some processes are protected by patents in different countries.

The Laboratories of this Section have not remained indifferent to the problem and, conscious of its interest, they have developed a process for the self-catalytic deposition of nickel on different metallic substrates and very especially on aluminum and its alloys.

A detailed study of the chemistry of the reduction process of nickel by means of hypophosphorous ions in aqueus sclutions has enabled us to confirm the fact that the solutions have metastable character and are highly sensitive as far as they

are concerned to some substances the presence of which might inhibit the reaction. It is generally accepted that in the nickel reduction by means of hypophosphite ions the following reactions take place fundamentally:

$$N_{i}^{++} + PO_{2}H_{2}^{-} + H_{2}O \longrightarrow N_{i} + PO_{3}H_{2}^{-} + 2H^{+}$$
 (I)

$$PG_{2}H_{2}^{-} + H_{2}G \longrightarrow PG_{3}H_{2}^{-} + H_{2}$$
 (II)

being necessary, likewise, to admit other secondary reactions by means of which the hypophosphite ion is reduced to phosphorus since the reduced nickel contains it in variable proportions according to work conditions.

The reaction Eshows that there is a liberation of protons the concentration of which may reach such a value that could hinder the reduction of the Ni ++ ions. It will be necessary, in any case, a convenient buffer action to maintain the pH values within the adaquate limits for an extended utilization of the solutions. The reactions I and II show that the reduction of the Ni^{++} ions and the dehydrogenation of the hypophosphite ions convey to the formation of phosphite ions which limit considerably the use of the solutions since nickel phosphite is precisely insoluble at the more acceptable pH values of the process. The nickel phosphite produced in the reaction may form crystallization nuclei which besides producing defective deposits could cause the spontaneous decomposition of the solution. A conveniently formulated solution should contain, besides the nickel salts as source of nickel ions, complex forming agents capable of hindering the formation of basic nickel salts, a buffer system capable of maintaining the pH in optimum conditions during long work periods and capable likewise of maintaining in solution the nickel phosphite produced in the reaction, the presence of which is undesirable for the above mentioned reasons and which compels

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to a frequent if not continued filtration of the solutions which may create a serious problem when the phosphite does not reach the crystalline form.

Taking into consideration all that has previously been explained, as far as the reaction mechanism is concerned, as well as the conditioning of the metallic surfaces which receive self-cetalytic nickel deposits, our program is slearly differentiated as far as its objectives:

- 1 Formulation of the solutions capable of yielding selfcatalytic nickel deposits on different metallic substrates.
 This requires in its turn; end
 - a) Selection of the nickel salts, portable of nickel ions, with the necessary purity to guarantee the efficiency of the process as well in the initial preparation of the solutions as in its replacement in the needed amounts to maintain the Ni ions concentration at the adequate levals.
 - b) Selection of the complex forming agents, compatible with the nickel salt and the hypophosphite ion used as reducing agent, which will hinder the formation of basic salts as well as nickel phosphite and maintain the deposition rate within acceptable limits. The association of these components should have likewise, the sufficient buffer capacity to maintain the pH value within such limits that the reaction will not be sensibly affected.
 - c) Selection of stabilization system adequated to the composition of the solutions and the consumption rate of which might be exactly controlled. The stabilization should not sensibly effect the deposition rate and its yield.

- d) Selection of the necessary additives to reduce the porosity of the deposits or afford other properties and the presence of which in no case should sensibly either affect the deposition rate or the yield.
- 2 Selection of the surfaces conditioning process according to the proper characteristics of the base metal. The metallic surfaces conditioning is in any case a factor of primary importance in order to insure a successful protection. In the case of the self-catalytic nickel depositions the said surfaces conditioning reaches its highest requirements being, probably the aluminum and its alloys, the metal which presents the major problems and to which, in our work program, it has been devoted a special attention.

II - EXPERIMENTAL PART

1 - FORMULATION

The products used in the different solutions formulation for our experiments have been of the highest purity and its relation is the following:

Mickel carbonate; - CO3Ni 2Ni(OH), . 4H,O

Nickel sulfate; - SC₄Ni . 7H₂C

Nickel hypophosphite; - $(PO_2H_2)_2$ Ni.5H20

Citric acid; - C6H3O7.H2O

Glycolic acid; - C2H4C3

Hypophosphorous acid; $= PC_2H_3$ (50% in weight; specific gravity = 1.25)

Di-isopropanol-amine; - S6H15CNL

Ammonium hydroxide: - NH4CH

The nickel sulfate has been used only in those tests carried out to study the influence of the Ni^{o+} ions concentration

for a constant $PO_2H_2^-$ ions concentration.

The hypophosphorous acid has been used in those tests certisd out to study the influence of the $PR_2H_2^+$ ions concentration for a constant Ni^{**} ions concentration.

The nickel hypophosphite, $(PD_2H_2)_2Ni.6H_2\theta$ has been used when the joint replacement of Ni^{++} and $PD_2H_2^-$ ions has been required.

In our work, finally, two solutions have been selected, the composition and operating characteristics of which will be exposed further on, its performance has been found satisfactory, as concerning deposits quality, deposition rate and stability, exempt from sulfates and the replacement of which has only required the addition of nickel hypophosphite, hypophosphorous acid and a correct adjustment of the pH by means of ammonium hydroxide.

The preparation of the base solutions for our experiments includes the following phases:

- Dilution of the acid (citric or glycolic) in distilled water.
- Nickel carbonate addition in small portions with constant stirring until complete dilution.
- Addition of a 50% solution of di-isopropanol-amine.
- Filtration over whatman paper nº 42.
- Hypophosphorous acid addition.
- Addition of ammonium hydroxide until obtaining the working pH.
- Dilution with distilled water up to expected final volume.

The amounts of each component, the relation of which has been exposed, have been in every case the necessary ones to reach the expected concentrations in our experiments.

2 - PANELS

The variables of the deposition process (components concentration, temperature, pH, stirring, etc.), until obtaining the setting up of the proper solutions, have been studied amploying laminated in cold F-lll steal panels. Once the most satisfactory formulations were obtained, the process has been carried out on copper, aluminum and L-3140 alloy panels.

2.1. Steel panels conditioning.

In all our tests the steel panels were submitted to a cleaning treatment in trichloroethylene chamber followed by an alkaline fat removal process through immersion in a solution with the following composition:

Being the working temperature in the range 35....
90%C during 15 ... 20 min. with strong stirring.
The panels were subsequently rinsed with tap water
first and then with distilled water, afterwards
they wey were subjected to an activation process
by immersion at room temperature in a solution
with the following composition:

during 4 ... 3 minutes. After being rinsed with

tap and distilled water the panels were introduced in the self-catalytic mickel solution.

Cther steal surfaces conditioning methods have been tested in our Laboratories and likewise with satisfactory results. The electrolytic pickling in sulfuric acid solutions and the immersion in concentrated sulfuric acid are among them, preceded in any case, by the above mentioned cleaning process. We do not object its utilization but we must emphasize the fact that the self-catalytic nickel deposition, being specially indicated on parts with complicated conformation, could be conditioned by a conditioning of the surfaces of doubtful afficiency in this respect.

2.2. Copper panels conditioning.

In all our tests the electrolytic copper panels were subjected to a fat removal process in trichloroethy-lene chamber followed by a chemical polishing through immerssion in a solution with the following composition:

at 50...65°C during 2...4 min. The panels were rinsed with tap water and afterwards with distilled water and introduced in the self-catalytic nickel solution.

Other chamical polishing processes such as the immersion in sulfuric acid/potassium dichromate solutions have been used in our laboratories with equally satisfactory results.

2.3 Aluminum and L-314C alloy panels conditioning.

The sequences which constitute the aluminum and L-3140 alloy surfaces conditioning followed in these Laboratories are the following:

- Fat removal in trichloroethylene chamber.
- Immersion in an alkaline solution with the following composition:

Anhydrous Sodium Carbonate 5C gm/l.

Sodium hydroxide 1C gm/l.

Triethanolamine (TEA) 2C gm/l.

Sodium nitrite 13 gm/l.

at 35 ...90°C during 3...5 minutes.

- Rinsing with tap water followed by rinsing with distilled water.
- Immersion in nitric acid 1:1 (by volume) during 5 minutes at room temperature.
- Rinsing with tap water followed by rinsing with destilled water.
- Immersion in a zincate solution with the following composition:

Triethylene tetramine (TETA) 300 mil.

Triethanolamine (TEA) 100 "

Sodium hydroxida 50 gm.

Zinc oxide 45 "

Matar up to 1 liter

The dilution of the zinc exide is slow and requires

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a strong stirring at room temperature.

The zincate was carried out at 35...90°C during 30...60 sec.

- Rinsing with tap water followed by a careful rinsing with distilled water.
- Immersion in the self-catalytic nickel solution.

2.3.1 Commentaries:

The conditioning of the aluminum and L-3140 alloy panels followed in our Laboratories present peculiarities as a consequence of the specific characteristics of the base metal which we consider convenient to comment.

The treatment in the alkaline solution, the composition and working conditions of which were exposed, produces on the L-3143 allow panels obscure sludges slightly adhesive and, in any case, easily soluble in 1:1 nitric acid solution.

The loss of material is minimal and the state of the surfaces is completely satisfactory to receive the following zincate treatment.

The zincate process developed in our laboratories presents remarkable differences in contrast to the conventional method known as "double zincate". The solution used in our process contains a high zinc concentration due to the presence of TETA and TEA which at the same time prevents, to a certain degree, the precipitation of the aluminum hydroxide eventually formed, being easily sliminated by filtration if its presence takes place as a consequence of the long use of the solution.

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The sodium hydroxide concentration is considerably lower than the one of the conventional solutions and the risk of carbonatation is therefore diminished so that the useful life of the solution is appreciably longer.

Our experiments have shown that the replacement of the spent zinc may be done with periodical additions of a solution with the following composition:

Being necessary to carry out the previous analytical determination of the Zn to maintain in at the concentration already indicated in the process stages, determination which, on the other hand, does not present major difficulties following the conventional analytical methods.

Our experiments have likewise demonstrated that it is sufficient only one immersion in the zincate solution to obtain satisfactory deposits with which the "double zincate" is eliminated, the mechanism of which is not satisfactorily explained.

The zinc deposits obtained by immersion in the solution, the formulation and working conditions of which we indicated, present a great adhesion in contrast with the adhesive tape and its perosity is inappreciable in contrast to the immersion test in boiling water during I hour.

We must emphasize the fact that the zincate process

followed in our laboratories for the aluminum and L-3140 alloy panels conditioning does not exclude the possibility of using the "double zincate" process for the deposition of the self-catalytic nickel by means of the process developed likewise in these Laboratories. At the same time we consider important to point out that the zincate process carried out in our Laboratories is apt to receive self-catalytic nickel deposits coming from commercial firms as our experience has demonstrated.

In table I the results obtained in a series of tests carried out on aluminum and L-314G alloy are shown, where the following data are considered: the material loss, the weight of the zinc deposit and its thickness with regard to the immersion time. In all the cases the working temperature has been of 35... 90° C on panels with 1 dm² and in a solution volume of 1 liter.

TABLE I

Panel	Time (min.)	Weight loss (gm)	Daposited Zn (gn)	Thickness
Aluminum	1	0.005	0.026	0.29
Aluminum	2	0.015	2.050	2.75
Aluminum	3	C.929	2.960	7.34
L-3140	1	0.005	0.020	0.29
L-3140	2	0.010	0.040	0.56
L-3140	3	3.326	0.065	0.91

It can be seen that the material loss is minimum and that the rears no substantial differences between the aluminum and the L-3140 alloy; it can be preserved likewise that the

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zinc deposit increases with the immersion time. This characteristic is very important since although the zinc deposits are equally uniform, adhesive and free of pores, independently of their thickness, the self-catalytic nickel deposits are defective when the zinc deposit is high; which compels to work with small thickness deposits, times of 30...60 seconds of immersion in the zincate solution being sufficient. The interpretation we give to this fact is the following: The zinc layer protects the aluminum and its alloys from their oxidation in the presence of air but the self-catalytic nickel deposition does not take place on the zinc layer since it is dissolved when introduced in the nickel solution on working conditions. It is then necessary for the zinc layer to have the sufficient thickness to hinder the aluminum oxidation and at the same time that the said thickness be the minimum in order that its dilution in the nickel solution may rapidly take place and the nickel deposition may take place on the aluminum surface totally free of oxide. It is possible then that, upon the initiation of the reaction a zinc codeposition could eventually take place but not a superposition of layers. In all our tests we have observed that the reaction takes place immediately and that in the first minutes the nickel deposit is black and acquires the proper color of this metal during the course of the reaction.

The immersion in the self-catalytic nickel solution should immediately follow the zincats of the panels. We want to consider also here as valid the above mentioned argument since in many tests carried out, it has been pointed out that the zinc layers exposed to the air during long periods of time present a greater chemical inertia to the nickel solution than the more recently obtained ones.

The gind layers obtained by means of the process we have

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described in 2.3 are light gray, uniform, adhesive and non porous even with high thicknesses. Nevertheless, we insist that the immersion times should be between 30 and 60 seconds in order to obtain satisfactory nickel deposits since the zinc layer is rapidly dissolved by the mickel solution.

3 - NICKEL DEPOSITION

3.1 Working conditions.-

We describe below the conditions under which the work has been carried out for the obtainment of nickel deposits starting from two solutions the composition of which are indicated further on.

- In all our tests we have worked with a 2 liter solution contained in high glass flasks and the heating was produced by electric plate.
- The homogenization of the solutions during all the treatment has been carried out by magnetic stirring.
- The panels were suspended by means of iron wire during the treatment. In these conditions the copper panels immediately receive the nickel as a consequence of the potential difference established between both metals in contact.
- Plane rectangular panels were used, of 0.5 and 1.0 dm² of surface, the nature and conditioning of which has been described in 2, with the purpose of evaluating the effect of the C/V relation on the deposition.
- Special attention has been paid to a rigorous control of the pH and working temperature.

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3.2 Composition ot the solutions.

In our work, two typical solutions have been used, the composition of which is indicated below, and which were formulated as it was shown in II.

Solution A

Ni **	3.1 gm/l	(0.14 M).
Slycolic acid	50.0 "	(0.63 M).
Di-isopropanol-amine	20.0 "	(3.15 ⋈).
Hypophosphorous acid	10.0 ".	(0.15 M).
Additive 1	15 p.p.m.	
Additive 2	G.5 gm.	
Ammonium hydroxide	until pH :	= 4.3.
Temp.= 35	9010	

Solution E

N2 **	3.1	gm/l	(C.14	X).
Glycolic acid	40.C	***	(0.50	图)。
Citric acid	15.0	19	(3.07	\mathbb{N}).
Di-isopropanol-amine	20.0	11	(0.15	м).
Hypophosphorous acid	10.0	Ħ	(3.15	M).
Additive 1	15 p.	p.m.		
Additive 2	9.5	gm.		
Ammonium Hydroxide	until	L pH :	= 4.3.	
Temp. = 35	. 9920	:		

3.3 Sotainment of deposits.

The composition of the solutions which we have indicated constitutes the starting base for our tests and with which completely satisfactory results have been obtained. The deposition rate, in both solutions, does not show significant differences (15...20 microns/hr) and the aspect of the deposits do not show significant differences either. In both solutions the yield (consumption of $PC_2H_2^2/gm$ of deposited nickel) remains within the same limits (3.5 ... 4.5).

The solutions are stable and the deposition rate keeps within acceptable values during long periods of use with the adequate raplacement of $\text{Mi}_{\bullet}^{\bullet \bullet}$ $PS_2^{H_2^-}$ and additive 1 to maintain the concentration of these at its initial value. In our experiments we have been able to confirm that such deposition rate is reduced to 3 ...10 microns/hr. when there were already deposited 15 ... 20 gm of nickel per liter of solution.

At no time, during the use of the solutions until the above mentioned nickel deposition was reached, the nickel phosphite formation could be estimated and the slight diminution of the pH, in every test, has demonstrated that the solutions are well buffered and the complex forming agents are highly efficient to hinder the precipitation of basic salts and of phosphits.

In some tests the deposition of metallic mickel has been verified, firmly adhered on the bottom of the flask precisely in the zone where the magnetic stirrer has caused an abrasion of the glass and

where a superheating of the solution must occur.

This circumstance may be avoided employing another heating and stirring method.

The eventual presence of undesirable products (organic matter, dust, etc.) may be eliminated by means of treatment with active carbon followed with filtration through whatmen paper nº 42. This treatment requires the replacement of additives 1 and 2 since they are, likewise, eliminated by the active carbon.

The solutions have maintained themselves transparent and with an intense green color throughout the utilization time.

The reaction takes place immediately on the panels made with the materials and surface conditioning indicated in 2 using the suspension system indicated in 3.1.

In the zincated aluminum panels the reaction takes place, likewise, immediately upon being introduced in the solution with the consequent nickel deposition that in the first minutes has a black color acquiring afterwards the proper color of this metal. The interpretation given to this fact is that there is no nickel deposition on the zinc layer but a dilution of the latter with the possibility of a decoposition which takes place in a short period of time, the normal nickel deposition taking place afterwards. This aspect of the process has been already indicated in 2.3.1.

With the solutions employed in our tests, the composition of which is indicated in 3.2, the influence of the temperature and of the working pH does not present worth mentioning differences as compared with other

processes also tested in our Laboratorias. The deposition rate increases with the temperature and the pH. Never—theless, our experience recommends to work at temperatures of 35 ... 90°C and pH values of 4.5 ... 5.6. Although higher temperatures increase the deposition rate, they do, on the other hand, sugment the risk of decomposition and may considerably diminish the yield. The solutions are likewise assentially more unstable at higher pH than the ones indicated and below the inferior p^{μ} limit the deposition rate sensibly decreases also with an equally diminution of the yield.

The S/V relation is of utmost importance in a great many number of chemical conversion processes, electro-deposition, etc. but, probably, the self-catalytic deposition is the most exigent in this aspect. Our experiments have damonstrated that the lower this relation is, the higher is the quality of the nickel deposits.

We have considered as most satisfactory a maximum relation of $0.5 \, \mathrm{dm}^2/1$. In these conditions, an unbalanced relation of components is not produced and the buffer capacity of the solutions makes it possible to work with the above mentioned pH values, even with a long deposition.

With the solutions tested by us and in the conditions we have previously indicated, nickel thicknesses of more than 100 microns have been obtained, without interruption and without any more care than the proper replacement of the proper and Additive 1. In the tests carried out in our Laboratories we have been able to confirm the fact that the nickel layers require a reactivation when the process has been interrupted. In such a contingency the mentioned reactivation may be obtained by immersion at room temperature, in a 20% perchloric acid solution.

After a careful rinsing the penels should be inmediately

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introduced in the nickel solution. With this reactivation the adhesion between layers is completely satisfactory.

The deposition rate is notably influenced by the Mi and PO2H2 concentrations present in the solution; nevertheless, the values indicated in our formulations A and B have been found more convenient. Higher concentrations of $PS_2H_2^$ increase the deposition rate but with the consequent increment of the solutions instability and a decrease of the yield. An increase of the Ni ++ concentration unbalances the complex forming action of the products present in the solution and likewise the diminution of the mentioned concentration which makes considerably decrease the deposition rate as well as the yield. In table II the effect produced on the deposition rate by a variation of the Ni concentration, for a constant PB_2H_2 concentration may be estimated and in table III the effect produced, of the same characteristic, in solutions in which the Ni ++ concentration was maintained constant and variable the one of FC2H2. These values are the ones obtained with solutions in which 10 gm/l. of nickel had already been approximately deposited and in which, therefore, the $PC_3H_2^T$ concentration is high; They are then representative values of the deposition rate which may be obtained with average life solutions regarding the recently formulated solutions A and B.

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Mii** gm/l.	Deposition rats (microns/hr.)	
15.6	15.0	_
3.5	13.0	
3.6	12.0	
7.5	16.0	
7.0	3.5	
6.5	7.0	
5.0	6.0	
5.5	5.3	

TABLE III

Constant Ni ** concentration (6.2 gm/l.)

PS ₂ H ₂ gm/1.	Deposition mata (microns/hr.)
7.4	7.0
6.7	5.7
5.1	5.5
5.5	4.3
4.9	4.3

III - <u>CONCLUSIONS</u>

We consider that in our work program the objectives indicated in I-1 and I-2 have been satisfactorily reached. The solutions employed in our experiments, the composition and working conditions of which we indicated in II-3.1 and II-3.2, show a great stability, great buffer capacity and their utilization may be lengthened even with high concentrations of $FC_3H_2^-$ ion originated in the dahydrogenation of the $FC_2H_2^-$ ion. The nickel deposits are uniform and exempt of pores even with small thicknesses (IG...15 microns) independently of the nature of the base metal used in our tests. The bightness of the deposits increases with the thickness and this may reach great values provided the convenient component replacements are carried out.

We must insist in the fact that the surface conditioning is of vital importance in a successful deposition. As far as the aluminum surfaces conditioning is concerned, the sequences of which have been indicated in II-2.3, we consider that the process carried out in our Laboratories allow to obtain surfaces in proper conditions to receive self-catalytic nickel. With regard to this, we insist in our criterion that the zinc layer is dissolved in a short period of time upon introducing the panels in the nickel solution and that the nickel deposition occurs directly on the base matal and not over the zinc layer which, in any case, should have the sufficient thickness to hinder the aluminum oxidation and at the same time should be as small as possible to allow its rapid dilution. The fact that the zincate process studied in our Laboratorias may allow the self-catalytic mickel deposition in solutions coming from well known commercial firms confirm us its usefulness and has allowed us to establish the characteristics which should have a zinc deposit to receive layers of self-catalytic mickel (thickness, civaness and pompaity).

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The presence of In^{**} ions in the mickel solution does not seem to have significant effect on—the deposition rate, layer aspect, stability, etc. At least in the concentrations used in our experiments; this aspect of the process, regarding the presence of other metallic ions, has been expected in successive works.

We must emphasize the fact that the formulations used by us, as far as their composition are concerned, are not critical and allows a certain flexibility regarding the proportions of the glycolic and citric acids. The formulations with lactic acid in combination with the acids previously mentioned have been tried in our Laboratories and we hope, in our successive works, to be able to confirm our criterion of obtaining compromise formulations which would allow the obtainment of deposits with satisfactory characteristics.

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Alberto Cheriguian.

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